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A Comparative Study of Kinetics of Flotation of a Copper-Nickel Ore by N-Hydrocinnamoyl-N-Phenylhydroxylamine (HCNPHA) Vis-À-Vis Potassium Amyl Xanthate (PAX)

R. Natarajan* and **I. Nirdosh**

Department of Chemical Engineering, Lakehead University, Thunder Bay, Ontario, Canada P7B 5E1
** Present Address: Natural Resources Research Institute, University of Minnesota Duluth, 513 Miller Trunk Hwy, Duluth, MN 55811, USA*

Flotation kinetics was studied for the flotation of Canadian nickel ore using N-hydrocinnamoyl-N-phenylhydroxylamine (HCNPHA) as the collector. The differential flotation between pentlandite and pyrrhotite of HCNPHA was compared by repeating the experiments with potassium amyl xanthate (PAX). However, the pH for the flotation was 9.0 and 9.5, respectively, for using HCNPHA or PAX as collector. Time-recovery plots were fit using the modified first order rate equation for flotation kinetics, namely, $R_t = R_\infty e^{-k(t+\varphi)}$*, and flotation rate constant and the cumulative recovery at time infinite* (R_∞) *were computed. HCNPHA was found to react with pentlandite slightly faster than PAX. However, HCNPHA was found to float more pyrrhotite and silica than PAX thus the grade of the concentrates were adversely affected.*

INTRODUCTION

Hydroxamic acids are *N*-acyl derivatives of hydroxylamines and may be represented by a general structure R^1-N(OH)-C(=O)-R^2. Owing to their ability to form chelate complexes with several metal ions (Lutwick and Ryan, 1954; Shendrikar, 1969) they had been tested as mineral collectors in froth flotation, and classified as the O-O type chelating collectors. Pradip and Fuerstenau (1983, 1985, 1989, 1991) tested Alkylhydroxamic acids (R^1= H, and R^2 = alkyl) as collectors for oxidized copper minerals as well as for rare earth minerals (Fuerstenau and Pradip 1984). Yoon et al. (1992) reported the use of hydroxamates for the beneficiation of kaolin clay while Sreenivas and Padmanaban (2002) tested it to float cassiterite. A review by Nagaraj (1988) compiled all the early research on hydroxamic acids as mineral collectors. In the case of alkylhydroxamates structural modification is restricted to change in alkyl chain wherein it is impossible to change electronic properties of the chelating atoms by resonance. *N*-arylhydroxamic acids (R^1=aryl, and R^2= alkyl/aryl/aralkyl) are therefore better class of chemicals to study the effect of structure m on flotation efficiency (Natarajan and Nirdosh, 2001). Several *N*-arylhydroxamic acids were synthesized and tested for the flotation of a copper-zinc ore, and the effect of structure on the flotation efficiency was modeled using the Quantitative Structure-Activity Relationship (QSAR) approach (Natarajan and Nirdosh, 2003). In a similar study on the flotation of a copper-zinc ore using arylhydroxamic acids, Natarajan and Nirdosh (2006) observed flotation of sphalerite without activation by copper suphate and highlighted the economic importance of eliminating copper sulphate from the xanthate reagent scheme. The current paper explains the extension of the use of *N*-arylhydroxamic acids as mineral collectors to the beneficiation of nickel ores. Flotation of a Canadian nickel ore by *N*-hydrocinnamoyl-*N*-phenyl hydroxylamine (HCNPHA), also called *N*-phenyl hydrocinnamohydroxamic acid (see Figure 1 for structure) and the comparison of performance of the synthetic collector with that of potassium amyl xanthate (PAX) are reported here. Such a comparison of a synthetic collector with that used in the industry is necessary and very important to explore any industrial utilization of the new series of collectors to prevent it from getting dubbed as merely a wasteful academic exercise.

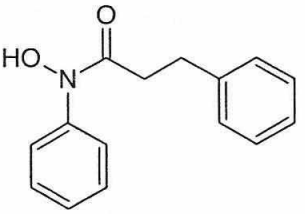
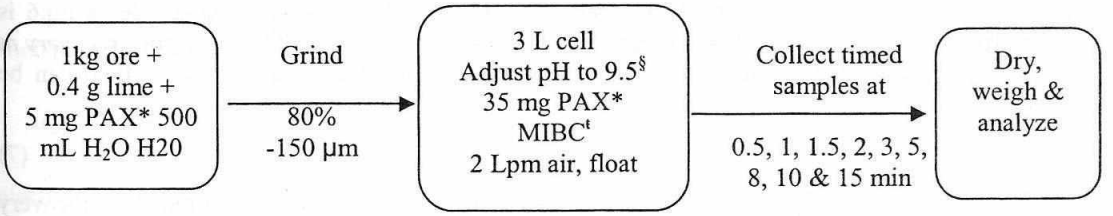


Fig. 1: Structure of HCNPHA

MATERIALS AND METHODS

Copper-nickel ore from INCO mines, Sudbury, Ontario, Canada was used in the experiments. The approximate ore composition was pentlandite 4-5%, chalcopyrite 4-5% and pyrrhotite 30-35%. The ore was ground in a polyurethane lined rod mill with stainless steel charge to avoid any external iron getting into the flotation system. HCNPHA which was found to give best mineral recovery in other studies (Natarajan et al 2004, Natarajan, Nirdosh 2006) was used in the current study. Synthesis and characterization of the compound are described elsewhere (Natarajan, Nirdosh 2006). A stock solution of HCNPHA was prepared by dissolving the solid in water and drops of 1% sodium hydroxide solution were added to completely dissolve the collector. An aqueous solution (0.1% w/w) of methyl isobutyl carbinol (MIBC) was used as frother. Lime water at the pH of the flotation test was occasionally added to the flotation cell to maintain the pulp level during the experiment. The details of the flotation experiments are outlined in Figure 2. Duplicate tests were performed for each flotation test to check the reproducibility of results. The flotation samples (floats and tails) were acid digested using HNO_3-HF mixture in Teflon crucibles and analyzed for copper, zinc and iron by inductively coupled argon plasma atomic emission spectrometer (ICAP).



* For HCNPHA tests PAX was replaced by HCNPHA (12 mg in grinding and 88 mg in flotation)
§ pH was adjusted to 9 when HCNPHA was the collector
For each experiment a duplicate test was done
t 10 mL of 0.1% (wt) solution was divided into 4 aliquots and added at different time intervals to maintain the level of frothing during collection

Fig. 2: Scheme to Show the Flotation (Kinetics) Experiments

RESULTS AND DISCUSSION

The basic equation of chemical kinetics for the rate of a reaction is:

$$rate = -\frac{dC}{dt} = kC^n \qquad (1)$$

where C is the concentration at time t, n is the order of the reaction, and k is the rate constant. When one applies this to froth flotation, C becomes the concentration of the floatable species (mineral(s)) at

time t. It is generally accepted that froth flotation follows first order kinetics, and n is equal to 1. The rate expression therefore becomes

$$-\frac{dC}{dt} = kC \tag{2}$$

This may be integrated over the limits

$$-\int_{C_0}^{C_t} dC = k\int_0^t dt \tag{3}$$

$$\ln\frac{C_o}{C_t} = kt \tag{4}$$

Eq.4 can be written as:

$$\frac{C_0}{C_t} = e^{kt} \tag{5}$$

On rearrangement:

$$C_0 - C_t = C_0(1-e^{-kt}) \tag{6}$$

C_0 in the above equation is the initial concentration of a particular mineral in the ore at time zero, i.e., the *maximum theoretically floatable amount* or the *theoretically maximum possible recovery* of the mineral. However, the complete recovery of the entire mineral present in the ore feed is never achievable because some mineral particles will be inaccessible due to their being locked inside other matrices such as quartz or in very coarse particles. Hence, C_0 on the right hand side of Eq.6 is replaced by the term R_∞, where R_∞ is the *maximum recovery achievable* or the *cumulative recovery at time infinite*. Noting that, C_0-C_t is equal to the cumulative recovery, R_t, at time t, Eq.6 can be rewritten as:

$$R_t = R_\infty(1-e^{-kt}) \tag{7}$$

A plot of cumulative recovery versus time is an asymptotic curve and the cumulative recovery corresponding to the asymptotic portion is the maximum recovery achieved, R_∞.

Agar (1985) considered two phenomena which are opposite in their action in affecting the flotation kinetics. Some solids in the slurry are naturally hydrophobic and will have air bubbles attached to them during the conditioning period. Hence, their flotation starts even before starting the air flow. On the other hand, when air flow is started, several seconds elapse before a full depth of loaded froth is present in the flotation cell. The first phenomenon gives a negative time correction while the second amounts to a positive time correction. Agar introduced a time correction factor φ in the above equation (Eq.7) for the first order flotation kinetics. The modified rate equation is:

$$R_t = R_\infty(1-e^{-k(t+\varphi)}) \tag{8}$$

The changes in flotation variables such as air flow rate and collector dosage change the numerical values of R_∞ and/or k. The effect of the variable on flotation is interpreted from the trend in the change of these parameters. However, in a situation where a given change in a flotation variable has opposite effects on the two parameters R_∞ and k, it becomes difficult to interpret the change in selectivity between a valuable mineral and a gangue mineral because selectivity is a combination of R_∞ and k. One usual way of simplification of situation was to assume $R_\infty = 1$, even though in practice $R_\infty < 1$. Xu (1998) suggested a modified rate constant K_M which is a combination of R_∞ and k and is

given by the equation:

$$K_M = R_\infty \times k \tag{9}$$

According to Eq.2

$$rate = C_t \times k$$

where C_t is the concentration of the mineral in the ore at time t.

When time $t = 0$, $C = C_0$

But $C_0 \approx R_\infty$

$$rate = R_\infty \times k \tag{10}$$

Hence, the modified rate constant K_M is the rate of the reaction at time $t = 0$. On partial differentiation of Eq.7 with respect to time:

$$R_\infty \times k = \left.\frac{\partial R}{\partial t}\right|_{t=0} \tag{11}$$

modified rate constant K_M, the product of R_∞ and k, is therefore the slope of the time cumulative recovery graph at time zero.

The modified rate constants were used by Xu to define a new quantity, selectivity index (SI) or the relative rate constant of one mineral (M_1) over the other mineral (M_2). It is the ratio of the modified rate constant of mineral M_1 to the modified rate constant of mineral M_2:

$$SI_{(M_1/M_2)} = \frac{K_M \ of M_1}{K_M \ of M_2} \tag{12}$$

When the selectivity index is calculated between a valuable mineral M and a gangue mineral G, then

$$SI_{(M/G)} = \frac{K_{M_M}}{K_{M_G}} \tag{13}$$

Selectivity index (SI) is the quantification of the selectivity of a collector for a particular mineral over the other under the given set of process variables. Factors having positive effect on SI have to be identified to maximize the separation between two minerals.

Table 1: Kinetic Parameters From Model Fit and Selectivity Index (SI)

Kinetic parameters	PAX (Test K-1)			PAX (Duplicate) (Test K-2)		
	Pn	**Cp**	**Po**	**Pn**	**Cp**	**Po**
R_∞	79.09	91.50	41.37	77.07	90.93	39.16
k	0.303	0.878	0.175	0.274	0.689	0.139
K_m	0.239	0.804	0.072	0.211	0.627	0.054
SI w.r.t. Po	3.31	11.10	1.00	3.87	11.49	1.00
	HCNPHA (Test K-3)			**HCNPHA Duplicate (Test K-4)**		
R_∞	80.42	93.24	51.16	75.29	92.53	41.05
k	0.316	0.825	0.161	0.358	0.854	0.225
K_m	0.254	0.769	0.0822	0.270	0.790	0.0923
SI w.r.t. Po	3.09	9.36	1.00	2.92	8.57	1.00

The time-recovery plots are shown in Figure 3 to Figure 4, and were fit for the modified rate equation (Eq. 8) to obtain the first order rate constant k and the recovery at infinite time R_∞. The rate constants and the modified rate constants for the minerals pentlandite (Pn), chalcopyrite (Cp) and pyrrhotite (Po) are listed along with R_∞ in Table 1. Selective index calculated for the valuable minerals Pn and Cp with respect to the gangue mineral Po are also given in Table 1.

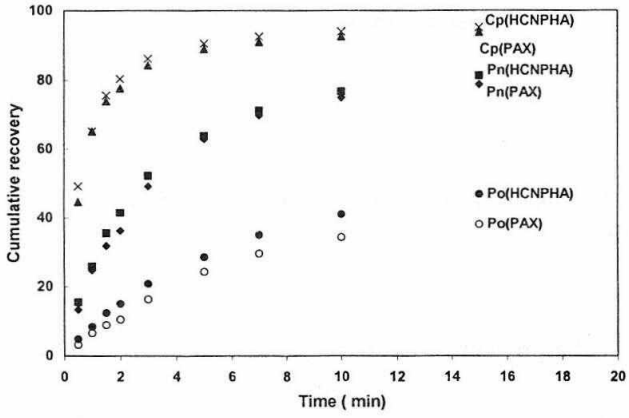


Fig. 3:Comparison of Flotation Kinetics of HCNPHA and PAX, Tests K1 and K3

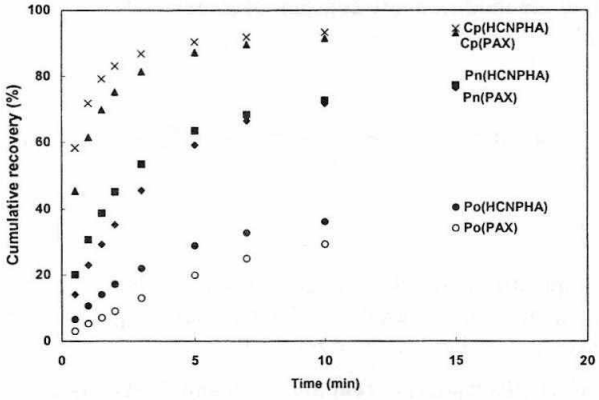


Fig. 4: Comparison of Flotation Kinetics of HCNPHA and PAX, Tests K2 and K4

The time-recovery curves in the Figures 3 and 4 and the parameters calculated from them show the good reproducibility of the test results HCNPHA and PAX recovered almost the same amount of pentlandite and chalcopyrite with a higher value of K_M for HCNPHA than that for PAX. This indicates that HCNPHA is a better collector for pentlandite. However, when flotation of pyrrhotite is considered, HCNPHA floated more pyrrhotite than floated by PAX. Thus, the higher quantity of pyrrhotite floated by HCNPHA decreased its selectivity index, even though R_∞ and K_M values were favorable. Thus, suppression of pyrrhotite is essential and which will make HCNPHA undoubtedly a better collector than PAX. Another very important observation that supports the claim of the potential candidacy of HCNPHA is its faster kinetics in the flotation of pentlandite. In both the sets of experiments, the first order rate constant k for pentlandite flotation by HCNPHA was found to be higher than that by PAX

Though the recoveries and the rates of flotation, their combined measure selectivity index are to be considered in flotation efficiency of a collector, the other important factor to be considered is the

grades of floats. The plots of pentlandite recovery against grade of the concentrate (cumulative Cu + Ni grade) for the two sets of experiments are given in Figure 5 for all the four tests. PAX was found to perform better than HCNPHA but the difference between them was not very high. Inefficient suppression of the gangue minerals, namely pyrrhotite and silica was responsible for the lower grades of concentrates floated by HCNPHA.

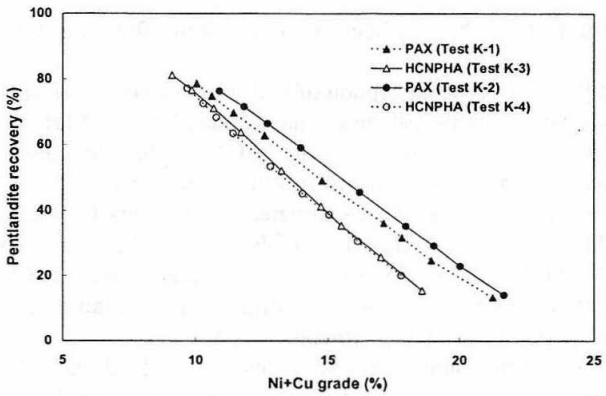


Fig. 5: Pentlandite Recovery Vs Concentrate (Ni+Cu) Grade

CONCLUSION

The results indicated that HCNPHA floated pentlandite and the mineral recovery was as good as achieved with PAX. The kinetics of flotation of pentalndite by HCNPHA was slightly faster than that by PAX, and this was indicated by rate constants. However, HCNPHA floated more silica and pyrrhotite than PAX this affected the nickel grade of the concentrate. The new synthetic collector was tested using the reagent system developed for xanthates. A new reagent system involving modifiers, frothers etc., is to be evolved for the new series of collectors and this follow up research is very important for developing a new reagent system alternative to xanthate system.

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